Viscoelastic properties of thermoreversible gels formed by telechelic associating polymers

AUTHOR(S):

Indei, Tsutomu

CITATION:

Indei, Tsutomu. Viscoelastic properties of thermoreversible gels formed by telechelic associating polymers. 物性研究 2006, 87(1): 160-161

ISSUE DATE:

2006-10-20

URL:

http://hdl.handle.net/2433/110597

Viscoelastic properties of thermoreversible gels formed by telechelic associating polymers

Fukui Institute for Fundamental Chemistry, Kyoto Univ. Tsutomu Indei [1]

[概要] 温度・濃度等の変化に伴い可逆的にゾル・ゲル転移を起こすゲルを可逆ゲルと呼ぶ．本研究では，両末端に会合基を有するテレケリック会合高分子が形成する可逆ゲルの，ポストゲル領域における粘弾性を論じる．

1 Introduction

Viscoelastic properties of thermoreversible gels whose junctions are formed by the clustering of an arbitrary number of functional groups on telechelic polymers are theoretically studied by developing the transient network theory by Tanaka and Edwards so that the aggregation number of the junction can be treated. In this work, we focus on linear viscoelasticity of thermoreversible gels, and the results are compared with experimental data observed for telechelic poly(ethylene oxide).

2 Theory

Let $F_{k,k'}(\mathbf{r},t)$ be the number of (k,k')-chains $(k,k'=1,2,3\cdots)$ at time t having the end-to-end vector $\mathbf{r}$. The (k,k')-chain is defined as the chain whose one end is incorporated into the junction formed by k functional groups whereas the other end is connected with the junction comprised of k' groups. $F_{k,k'}(\mathbf{r},t)$ satisfies the following evolution equation:

$$\frac{\partial F_{k,k'}(\mathbf{r},t)}{\partial t}+\nabla\cdot(P_{k,k'}\hat{\kappa}\mathbf{r}F_{k,k'}(\mathbf{r},t))=W_{k,k'}(\mathbf{r},t), \tag{1}$$

where $P_{k,k'}$ is the probability that the (k,k')-chain is elastically effective, and $\hat{\kappa}$ is the rate of deformation tensor applied to the system. The right-hand side is a reaction term that describes the net increment of (k,k')-chains due to the reaction between the functional group on the (k,k')-chain and the junction. In equilibrium, (1) reduces to $\psi_k=K_k\psi_1^k$ (ψ_k is the volume fraction of functional groups belonging to junctions formed by k functional groups; K_k is the reaction constant). Once $F_{k,k'}(\mathbf{r},t)$ is obtained by solving (1), we can have the shear stress $\sigma_{k,k'}$ ascribed to (k,k')-chains by making use of the formula: $\sigma_{k,k'}=(3k_BT/Na^2)\int d\mathbf{r}xyF_{k,k'}(\mathbf{r},t)$ (N is the number of the repeat unit of the chain, a is the length of the repeat unit, k_B is the Boltzmann constant and T is the temperature). The total (observable) stress is then given by $\sigma=\sum_{k,k'}\sigma_{k,k'}$.

[1]E-mail: indei@fukui.kyoto-u.ac.jp

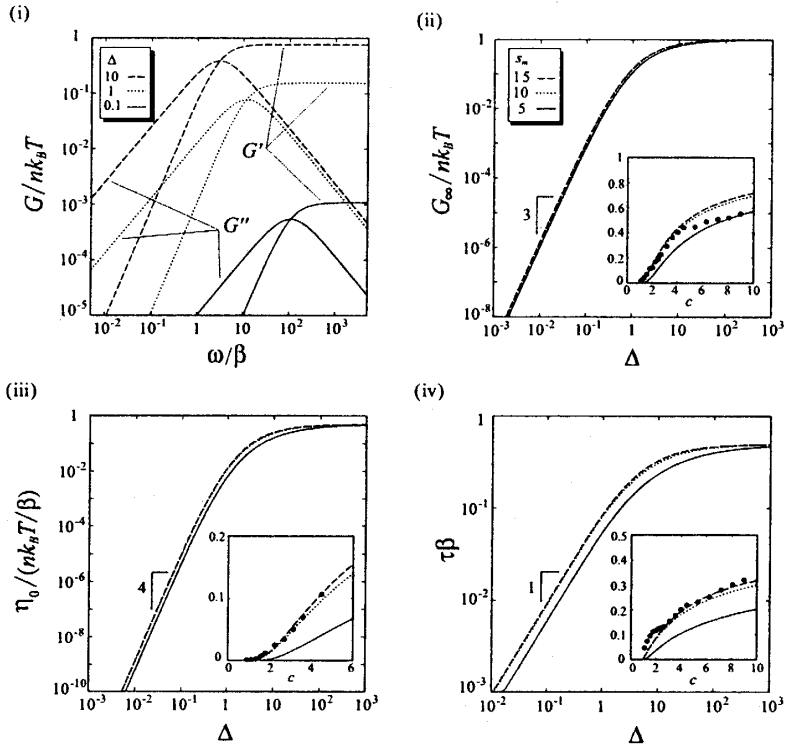

Figure 1: (i) The dynamic shear moduli reduced by nk_BT (n is the total number of chains per unit volume) as a function of the frequency (divided by the dissociation rate β of the functional group). The relative concentration deviation $\Delta = (c - c^*)/c^*$ from the sol/gel transition concentration c^* is varying from curve to curve, while the maximum multiplicity of the junction is fixed at $s_m = 15$. (ii) The reduced plateau modulus, (iii) the reduced zero-shear viscosity ($\beta = 2$ sec^{-1}), and (iv) the unitless relaxation time plotted against Δ. The maximum multiplicity is varying from curve to curve. The insets of (ii) $\sim$ (iv) show the linear plot of each quantity as a function of the reduced polymer concentration c compared with experimental data (filled circles) for telechelic poly(ethylene oxide) in water obtained by Annable *et al.* [J.Rheol. **1993**, *37*, 65]. Experimental data are horizontally shifted by a factor of 0.9.

3 Results

Fig.1 shows the dynamic-mechanical and viscoelastic properties of the present system. The dynamic shear moduli are well described by the Maxwell model with a single relaxation time. The concentration dependence of the plateau modulus $G_\infty = G'(\omega \to \infty)$, the zero-shear viscosity $\eta_0 = \lim_{\omega \to 0} G''(\omega)/\omega$, and the relaxation time τ obtained from the peak position of $G''(\omega)$ are also shown in Fig.1. We see that the critical behavior of these quantities obey the mean-field scaling law; $G_\infty \sim \Delta^t$ with $t = 3$, $\eta_0 \sim \Delta^k$ with $k = 4$, and $\tau \sim \Delta^x$ with $x = 1$ irrespective of the value of the maximum multiplicity s_m (the junction can be formed by any number of functional groups less than or equal to s_m). Theoretical curves with large s_m can fit well with experimental data if we choose the adequate values for two parameters (i.e., the dissociation rate β of the functional group and the scaling factor for the concentration axis).